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TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371				Mo-5726/LeA 32,563	
				U.S. APPLICATION NO. (If known, see 37 CFR 1.51) <b>09/555921</b> To be assigned	
INTERNATIONAL APPLICATION NO. PCT/EP98/07753		INTERNATIONAL FILING DATE December 1, 1998		PRIORITY DATE CLAIMED December 13, 1997	
TITLE OF INVENTION METHOD FOR PRODUCING THERMOPLASTIC POLYURETHANE ELASTOMERS					
APPLICANT(S) FOR DO/EO/US Wolfgang Kaufhold; Friedemann Müller; Wolfgang Bräuer; Ulrich Liesenfelder; Herbert Heindingsfeld					
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:					
<ol style="list-style-type: none"> <li>1. <input checked="" type="checkbox"/> This is a FIRST submission of items concerning a filing under 35 U.S.C. 371.</li> <li>2. <input type="checkbox"/> This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371.</li> <li>3. <input checked="" type="checkbox"/> This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).</li> <li>4. <input checked="" type="checkbox"/> A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.</li> <li>5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371(c)(2)) <ol style="list-style-type: none"> <li>a. <input checked="" type="checkbox"/> is transmitted herewith (required only if not transmitted by the International Bureau).</li> <li>b. <input type="checkbox"/> has been transmitted by the International Bureau.</li> <li>c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US).</li> </ol> </li> <li>6. <input checked="" type="checkbox"/> A translation of the International Application into English (35 U.S.C. 371(c)(2)).</li> <li>7. <input type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)) <ol style="list-style-type: none"> <li>a. <input type="checkbox"/> are transmitted herewith (required only if not transmitted by the International Bureau).</li> <li>b. <input type="checkbox"/> have been transmitted by the International Bureau.</li> <li>c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired.</li> <li>d. <input type="checkbox"/> have not been made and will not be made.</li> </ol> </li> <li>8. <input type="checkbox"/> A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).</li> <li>9. <input checked="" type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).</li> <li>10. <input type="checkbox"/> A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).</li> </ol>					
Items 11. to 16. below concern document(s) or information included:					
<ol style="list-style-type: none"> <li>11. <input type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98.</li> <li>12. <input checked="" type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.</li> <li>13. <input checked="" type="checkbox"/> A FIRST preliminary amendment. <input type="checkbox"/> A SECOND or SUBSEQUENT preliminary amendment.</li> <li>14. <input type="checkbox"/> A substitute specification.</li> <li>15. <input type="checkbox"/> A change of power of attorney and/or address letter.</li> <li>16. <input checked="" type="checkbox"/> Other items or information: Preliminary Amendment w/Abstract; PTO Form 1449 and references listed therein</li> </ol>					

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09/555921

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PATENT APPLICATION  
Mo-5726  
LeA 32,563

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

APPLICATION OF )  
WOLFGANG KAUFHOLD ET AL ) PCT/EP98/07753  
SERIAL NUMBER: TO BE ASSIGNED )  
FILED: HEREWITH )  
TITLE: METHOD FOR PRODUCING )  
THERMOPLASTIC POLYURE- )  
THANE ELASTOMERS )

**PRELIMINARY AMENDMENT**

Assistant Commissioner for Patents  
Washington, D.C. 20231

Sir:

Prior to the examination of the application, kindly amend the enclosed English language translation thereof as follows:

Please delete the title of the translated document appearing in page 1 and insert therefor a revised title reading: --Method for Producing Thermoplastic Polyurethane Elastomers--; also, in page 18, a page containing an abstract, delete the title and the word "Abstract" and insert therefor:

--Method for Producing Thermoplastic Polyurethane Elastomers

Abstract of the Disclosure --.

**IN THE CLAIMS:**

Please cancel Claim 8.

"Express Mail" mailing label number EK983331736US  
Date of Deposit June 6, 2000

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Donna J. Veatch

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REMARKS


The amendment renders the translated application in better conformance with U.S. practice. A page containing the amended Abstract of the Disclosure is enclosed.

An early examination on the merits is respectfully solicited.

Respectfully submitted,

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**Process for preparing thermoplastic polyurethane elastomers**

5 The present invention relates to a process for preparing thermoplastic polyurethane elastomers, the products resulting therefrom and their use.

10 Thermoplastic polyurethanes (TPU) are used very widely because they have good elastomer properties and can be readily processed. A very wide range of mechanical properties can be produced by suitable selection of the components. A review of TPUs, their properties and applications is given e.g. in Kunststoffe 68 (1978) 819, Kautschuk, Gummi, Kunststoffe 35 (1982) 569; G. Becker, D. Braun: Kunststoff-Handbuch, vol. 7 "Polyurethane" Munich, Vienna, Carl Hanser Verlag 1983. A review of methods of preparation is given in Plastikverarbeiter 40 (1989).

15 TPUs are generally built up from linear polyols, such as polyesterpolyols or polyetherpolyols, organic diisocyanates and short chain, generally difunctional, alcohols (chain lengtheners). They may be prepared batchwise or continuously.

20 The continuous extrusion process has been known for some time. In this process the starting materials are metered into a screw reactor, polycondensed there and then converted into a uniform granular form (US-A 3 642 964, DE-C 23 02 564, DE-C 25 49 371, DE-A 32 30 009, EP-A 31 142).

25 The extrusion process is comparatively simple, but has the disadvantage that the starting materials are mixed only in the reactor and under conditions under which polyaddition occurs extensively, which means that inhomogeneities and thus undesired, and uncontrollable, secondary reactions may occur.

30 EP-A 554 718 and EP-A 554 719 propose improving the extrusion process by feeding the starting materials into a nozzle and mixing them before entrance to the extruder. Since however the polyaddition reaction occurs only in the extruder, the

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products resulting from this process also have inhomogeneities which become obvious in particular in extrusion products such as films.

5 Methods of preparation are also known from the prior art in which the starting materials are first mixed in a mixing zone at temperatures at which no polyaddition takes place and then reacted with each other in a reaction zone which has the desired reaction temperature. The mixing and reaction zones are preferably designed as static mixers (DE-A 28 23 762, EP-A 747 409, EP-A 747 408).

10 It has now been found that TPUs with improved homogeneity and improved melting characteristics can be obtained when the difference between the temperatures of the starting materials used to prepare them is as small as possible prior to the mixing process.

15 Therefore the invention provides a process for the continuous preparation of thermoplastic polyurethane elastomers, in which

one or more organic isocyanates (A) and

20 a mixture (B) containing Zerewitinoff-active hydrogen atoms, comprising

25 B1) 1 to 85 equivalent-%, with respect to the isocyanate groups in (A), of one or more compounds with on average at least 1.8 Zerewitinoff-active hydrogen atoms and an average molecular weight  $\overline{M}_n$  of 450 to 10000,

30 B2) 15 to 99 equivalent-% (with respect to the isocyanate groups in (A)) of one or more chain lengthening agents with on average at least 1.8 Zerewitinoff-active hydrogen atoms and a molecular weight of 60 to 400, and

0-20 wt.%, with reference to the total amount of TPU, of further auxiliary agents and additives (C)

are homogeneously premixed in a reactor within a period of at most 5 seconds, wherein the difference between the temperatures of components (A) and (B), before entering the reactor, is  $< 20^{\circ}\text{C}$ .

Organic isocyanates (A) which may be used include aliphatic, cycloaliphatic, araliphatic, aromatic and heterocyclic polyisocyanates or any mixtures of these polyisocyanates (see HOUBEN-WEYL "Methoden der organischen Chemie", vol. E20 "Makromolekulare Stoffe", Georg Thieme Verlag, Stuttgart, New York 1987, p. 1587-1593 or Justus Liebigs Annalen der Chemie, 562, pages 75 to 136).

The following may be mentioned individually, by way of example: aliphatic diisocyanates such as ethylene diisocyanate, 1,4-tetramethylene diisocyanate, 1,6-hexamethylene diisocyanate, 1,12-dodecane diisocyanate, cycloaliphatic diisocyanates such as isophorone diisocyanate, 1,4-cyclohexane diisocyanate, 1-methyl-2,4-cyclohexane diisocyanate and 1-methyl-2,6-cyclohexane diisocyanate as well as the corresponding mixtures of isomers, 4,4'-diisocyclohexylmethane diisocyanate, 2,4'-dicyclohexylmethane diisocyanate and 2,2'-dicyclohexylmethane diisocyanate as well as the corresponding mixtures of isomers, also aromatic diisocyanates such as 2,4-toluylene diisocyanate, mixtures of 2,4-toluylene diisocyanate and 2,6-toluylene diisocyanate, 4,4'-diphenylmethane diisocyanate, 2,4'-diphenylmethane diisocyanate and 2,2'-diphenylmethane diisocyanate, mixtures of 2,4'-diphenylmethane diisocyanate and 4,4'-diphenylmethane diisocyanate, urethane-modified liquid 4,4'-diphenylmethane diisocyanate or 2,4'-diphenylmethane diisocyanate, 4,4'-diisocyanatodiphenylethane-(1,2) and 1,5-naphthylene diisocyanate. 1,6-hexamethylene diisocyanate, 1,4-cyclohexane diisocyanate, isophorone diisocyanate, dicyclohexylmethane diisocyanate, diphenylmethane diisocyanate isomeric mixtures with a 4,4'-diphenylmethane diisocyanate content of more than 96 wt.% are preferably used, in particular 4,4'-

diphenylmethane diisocyanate and 1,5-naphthylene diisocyanate. The diisocyanates mentioned may be used separately or as mixtures with each other. They may also be used together with up to 15 mol.% (calculated from the total diisocyanate content) of a polyisocyanate, but the maximum amount of polyisocyanate added should be only enough to produce a product which can still be thermoplastically processed. Examples of polyisocyanates are triphenylmethane-4,4',4''-triisocyanate and polyphenyl-polymethylene-polyisocyanates.

Zerewitinoff-active compounds (B1) which are used for the process according to the invention are those with on average at least 1.8 to 3.0 Zerewitinoff-active hydrogen atoms and an average molecular weight  $\overline{M}_n$  of 450 to 10000.

Compounds included here are, in addition to compounds which possess amino groups, thiol groups or carboxyl groups, are compounds with in particular 2 to 3, preferably 2 hydroxyl groups, in particular those with average molecular weights  $\overline{M}_n$  of 450 to 6000, especially those with an average molecular weight  $\overline{M}_n$  of 600 to 4500, e.g. polyesters, polyethers, polycarbonates and polyesteramides containing hydroxyl groups.

Suitable polyether diols may be prepared by reacting one or more alkylene oxides with 2 to 4 carbon atoms in the alkylene group with a starter molecule which contains two bonded, active, hydrogen atoms. The following may be mentioned as alkylene oxides: e.g. ethylene oxide, 1,2-propylene oxide, epichlorhydrin and 1,2-butylene oxide and 2,3-butylene oxide. Ethylene oxide, propylene oxide and mixtures of 1,2-propylene oxide and ethylene oxide are preferably used. The alkylene oxides may be used separately, alternately one after the other or as mixtures. The following may be used, for example, as starter molecules: water, aminoalcohols such as N-alkyl-diethanolamines, for example N-methyl-diethanolamine and diols such as ethylene glycol, 1,3-propylene glycol, 1,4-butanediol and 1,6-hexanediol. Optionally, mixtures of starter molecules may also be used. Suitable polyetherols are also hydroxyl group-containing polymerisation



products of tetrahydrofuran. Trifunctional polyethers may also be used in proportions of 0 to 30 wt.% with respect to the bifunctional polyethers, but at most in amounts such that a product which is still thermoplastically processable is produced. The substantially linear polyether diols preferably have average molecular weights  $\overline{M}_n$  of 450 to 6000. They may be used either separately or in the form of mixtures with each other.

Suitable polyester diols may be prepared, for example, from dicarboxylic acids with 2 to 12 carbon atoms, preferably 4 to 6 carbon atoms and polyhydric alcohols. The following are suitable, for example, as dicarboxylic acids: aliphatic dicarboxylic acids such as succinic acid, glutaric acid, adipic acid, suberic acid, azaleic acid and sebacic acid, or aromatic dicarboxylic acids such as phthalic acid, isophthalic acid and terephthalic acid. The dicarboxylic acids may be used separately or as mixtures, e.g. in the form of a succinic, glutaric and adipic acid mixture. To prepare polyesterdiols, it may optionally be advantageous to use the corresponding dicarboxylic acid derivatives such as diesters of carboxylic acids with 1 to 4 carbon atoms in the alcohol group, carboxylic acid anhydrides or carboxylic acid chlorides, instead of the dicarboxylic acids. Examples of polyhydric alcohols are glycols with 2 to 10, preferably 2 to 6 carbon atoms e.g. ethylene glycol, diethylene glycol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,10-decanediol, 2,2-dimethyl-1,3-propanediol, 1,3-propanediol or dipropylene glycol. Depending on the properties required, the polyhydric alcohols may be used separately or as a mixture with each other. Also suitable are esters of carbonic acid with the diols mentioned, in particular those with 4 to 6 carbon atoms, such as 1,4-butanediol or 1,6-hexanediol, condensation products of  $\omega$ -hydroxycarboxylic acids such as  $\omega$ -hydroxycaproic acid or polymerisation products of lactones, e.g. optionally substituted  $\omega$ -caprolactones. The following are preferably used as polyesterdiols, ethanediol-polyadipate, 1,4-butanediol-polyadipate, ethanediol-1,4-butanediol-polyadipate, 1,6-hexanediol-neopentylglycol-polyadipate, 1,6-hexanediol-1,4-butanediol-polyadipate and polycaprolactones. The polyesterdiols preferably have average molecular

weights  $\overline{M}_n$  of 450 to 6000 and may be used separately or in the form of mixtures with each other.

- 5 Zerewitinoff-active compounds (B2) are so-called chain lengthening agents and have on average 1.8 to 3.0 Zerewitinoff-active hydrogen atoms and have a molecular weight of 60 to 400. These are understood to include, in addition to compounds with amino groups, thiol groups or carboxyl groups, those compounds with two to three, preferably two hydroxyl groups.
- 10 Diols with 2 to 14 carbon atoms are preferably used as chain lengthening agents, such as e.g. ethanediol, 1,2-propanediol, 1,3-propanediol, 1,4-butanediol, 2,3-butanediol, 1,5-pentanediol, 1,6-hexanediol, diethylene glycol and dipropylene glycol. Also suitable however are diesters of terephthalic acid with glycols with 2 to
- 15 1,4-butanediol, hydroxalkylene ethers of hydroquinone, e.g. 1,4-di-( $\beta$ -hydroxyethyl)-hydroquinone, ethoxylated bisphenols, e.g. 1,4-di-( $\beta$ -hydroxyethyl)-bisphenol A, (cyclo)aliphatic diamines such as isophorone diamine, ethylene diamine, 1,2-propylene diamine, 1,3-propylene diamine, N-methyl-propylene-1,3-diamine, N,N'-dimethylethylene diamine and aromatic diamines such as 2,4-
- 20 toluylene diamine, 2,6-toluylene diamine, 3,5-diethyl-2,4-toluylene diamine or 3,5-diethyl-2,6-toluylene diamine or primary mono, di, tri or tetraalkyl substituted 4,4'-diaminodiphenyl methanes. Ethanediol, 1,4-butanediol, 1,6-hexanediol, 1,4-di-( $\beta$ -hydroxyethyl)-hydroquinone or 1,4-di-( $\beta$ -hydroxyethyl)-bisphenol A are particularly preferably used as chain lengtheners. Mixtures of the chain lengtheners mentioned
- 25 above may also be used. In addition small amounts of triols may also be used.

- Compounds which are monofunctional with regard to isocyanates may be used in amounts of up to 2 wt.%, with respect to TPU, as so called chain terminators. Suitable compounds are e.g. monoamines such as butyl and dibutylamine,
- 30 octylamine, stearylamine, N-methylstearylamine, pyrrolidine, piperidine or cyclohexylamine, monoalcohols such as butanol, 2-ethylhexanol, octanol,

dodecanol, stearyl alcohol, the various amyl alcohols, cyclohexanol and ethylene glycol monomethyl ether.

5 The substances which react with isocyanate must be selected in such a way that their average functionality does not exceed two if thermoplastically processable polyurethane elastomers are intended to be prepared. If higher functional compounds are used, the overall functionality must be lowered by means of monofunctional compounds.

10 The relative amounts of compounds (B1) and (B2) in (B) are preferably selected so that the ratio of the sum of isocyanate compounds in (A) to the sum of Zerewitinoff-active hydrogen atoms in (B) is 0.9 : 1 to 1.2 : 1, preferably 0.95 : 1 to 1.1 : 1.

15 Thermoplastic polyurethane elastomers according to the invention may contain up to a maximum of 20 wt.%, with respect to the total amount of TPU, of conventional auxiliary agents and additives as auxiliary agents and additives (C). Typical auxiliary agents and additives are catalysts, pigments, colorants, flame retardants, stabilisers against ageing and the effects of the weather, plasticisers, lubricants and mould release agents, substances which combat fungi and bacteria and fillers and  
20 mixtures thereof.

Suitable catalysts according to the invention are conventional tertiary amines known from the prior art such as e.g. triethylamine, dimethylcyclohexylamine, N-methylmorpholine, N,N'-dimethylpiperazine, 2-(dimethylamino-ethoxy)-ethanol,  
25 diazabicyclo[2.2.2]octane and the like and, in particular, also organic metal compounds such as titanates, iron compounds or tin compounds such as tin diacetate, tin dioctoate, tin dilaurate or the tin dialkyl salts of aliphatic carboxylic acids such as dibutyltin diacetate or dibutyltin dilaurate or the like. Preferred catalysts are organic metal compounds, in particular titanates, iron and tin  
30 compounds. The total amount of catalysts in the TPUs according to the invention is

generally about 0 to 5 wt.%, preferably 0 to 2 wt.%, with respect to the total amount of TPU.

5 Examples of other additives are lubricants, such as fatty acid esters, their metal  
soaps, fatty acid amides, fatty acid ester amides and silicone compounds, anti-  
blocking agents, inhibitors, stabilisers to protect against hydrolysis, light, heat and  
discoloration, flame retardants, colorants, pigments, inorganic and/or organic fillers  
and reinforcing agents. Reinforcing agents are in particular fibrous reinforcing  
10 agents such as e.g. inorganic fibres which are prepared in accordance with the prior  
art and may also be provided with a coating of size. More detailed data on the  
auxiliary agents and additives mentioned may be obtained from the specialist  
literature, for example from the monograph by J.H. Saunders and K.C. Frisch "High  
Polymers", vol. XVI, Polyurethane, part 1 and 2, Verlag Interscience Publishers  
1962 and 1964, Taschenbuch für Kunststoff-Additive by R. Gächter and H. Müller  
15 (Hanser Verlag Munich 1990) or DE-A 29 01 774.

Components (A) and (B) are mixed homogeneously in a reactor within a period of at  
most 5 seconds. The thorough mixing preferably takes place with a small amount of  
back-mixing. Homogeneous thorough mixing in the context of the invention means  
20 that the concentration distribution of components (A) and (B) and of the reaction  
product in the mixture has a relative standard deviation of less than 5 %. A small  
amount of back-mixing in the context of this invention means that the residence time  
in the reactor corresponds to that in a series of  $\geq 10$  ideal stirred tanks (stirred tank  
cascade).

25

Before components (A) and (B) are introduced continuously into the reactor, they  
must be heated, separately from each other, preferably in a heat exchanger, up to a  
temperature between 60 and 220°C, preferably between 90 and 190°C. According to  
the invention, it is essential that the temperatures of the two components (A) and (B)  
30 differ by less than 20°C before being introduced into the reactor. The temperature

difference between the component streams (A) and (B) is preferably  $< 10^{\circ}\text{C}$ , in particular  $< 5^{\circ}\text{C}$ .

5 The mixture obtained in this way is then converted into TPU in any type of reactor, preferably an extruder or a reaction tube.

10 According to the invention polyaddition is preferably performed in an insulated and preferably heatable static mixer. This has the advantage that it has no moveable parts and that homogeneous, thorough mixing with virtually no back-mixing can take place in the shortest possible time. Static mixers which can be used according to the invention are described in Chem.-Ing. Techn. 52, No. 4 on pages 285-291 and in "Mischen von Kunststoff und Kautschukprodukten", VDI-Verlag, Düsseldorf 1993.

15 Static mixtures in accordance with DE-C 23 28 795 are preferably used. The static mixers preferably have a length to diameter ratio of 8:1 to 16:1, in particular 10:1 to 14:1. The residence time in the static mixer is  $< 5$  seconds, preferably  $< 2.5$  seconds. The static mixers are preferably made from stainless steel, in particular from V4A.

20 In a further preferred embodiment, the process according to the invention is performed in a twin shaft extruder, whose shafts preferably rotate in the same direction. In this case the first part of the extruder can also be used to heat up the isocyanate component (A).

25 TPUs prepared by the process according to the invention may optionally be further processed, e.g. by annealing the polymer in the form of sheets or blocks, crushing or granulating in shredders or mills, degassing and granulating with melting. The polymer is preferably taken to a system for continuous degassing and extrudate production. This unit may be e.g. a multi-screw machine which if possible is provided with no kneading elements, or with only a few kneading elements.

30

The present invention also provides the thermoplastic polyurethane elastomers obtained using the process according to the invention. It has to be regarded as surprising that the moulding compositions prepared according to the invention have a high degree of homogeneity and improved melting characteristics.

5

Thermoplastic polyurethane elastomers obtained according to the invention are preferably used to prepare films and readily melted coextruded products such as laminates, calandered products, hot melt adhesives and for powder-slush coextruded products.

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## Examples

### Example 1

5

1630 g/h of MDI and 2685 g/h of a mixture of polybutanediol adipate (average molecular weight  $\overline{M}_n = 800$ ), which contained 200 ppm of a tin dioctoate, and butanediol in a ratio by weight of 6.9:1 were metered into a static mixer, separately from each other. The MDI and the polyol/butanediol mixture each had a temperature of  $140 \pm 10^\circ\text{C}$ . Premixing the components took place in a static mixer with all-round heating (model SMX, Sulzer AG) and with a diameter of 6 mm, a length of 6 cm and a rate of shear of  $500 \text{ s}^{-1}$ ; the reaction was performed in a reaction tube with mixing elements at the end.

15 Using this process, TPU could be produced for more than 90 minutes without a pressure increase being observed in the static mixer.

### Example 2

20 This test was performed in the same way as in example 1 with the difference that the temperature of the reactant streams was  $160 \pm 5^\circ\text{C}$ . Even under these conditions, TPU could be produced for more than 90 minutes without a pressure increase being observed in the static mixer.

### Example 3 (comparison)

25 The following temperature profile was preset in a reaction extrusion plant of the ZSK 83 type: housing 1-4:  $120^\circ\text{C}$ , housing 5-9: no temperature guidelines, housing 10-13:  $120^\circ\text{C}$ , head:  $200^\circ\text{C}$ . The same formulation as in example 1 was used, the rate of rotation was 300 rpm, the throughput 600 kg/h. MDI was metered into housing 1.

30

The temperature of the MDI at the entrance to housing 5 was about 90°C. The polyol/butanediol mixture with a temperature of 140°C was metered into housing 5.

The results of examples 1 and 2 and of comparison example 3 are given in Table 1.

- 5 The recrystallisation temperature was determined by DSC measurement with a calorimeter of the Perkin Elmer DSC 7 type. The product obtained in the comparison example had a peak maximum at a higher temperature during DSC measurement.

- 10 Whereas the melt flow index MFI for the TPUs prepared in the examples according to the invention increased by a factor of only 2 on increasing the temperature from 190°C to 200°C, this value increased by a factor of 5 in the comparison example. The low temperature dependence of the melt flow index MFI (ratio of MFI at 200°C to MFI at 190°C) and the higher MFI value of the TPUs prepared according to the invention indicate improved melting characteristics.

15

**Table 1**

	<b>Example 1</b>	<b>Example 2</b>	<b>Example 3 (comparison)</b>
Recrystallisation temperature $T_c$ [°C]	85	87	102
Melt flow index MFI ** (190°C)[g/10 min]	27	25	4.7
Melt flow index MFI ** (200°C)[g/10 min]	55	52	20.3

\*\* measured in accordance with ASTM D1238.

20

**Example 4 (comparison)**

The test was performed in the same way as example 1, but the temperature of the MDI at the entrance was 60°C and that of the polyol/butanediol mixture was 140°C.

- 25 After about 10-15 minutes, the pressure in the static mixer had already increased to >50 bar, so the experiment had to be terminated.



Using the industrially conventional high temperature difference of 80°C between the starting components, intense inhomogeneities are observed due to poor mixing. This leads to accretions in the static mixer due to cross-linking reactions or premature deposition of crystallites.

5

**Example 5**

1194 g/h of HDI and 3800 g/h of a mixture of polytetrahydrofuran (average molecular weight  $\overline{M}_n = 1000$ ) and butanediol in the ratio by weight of 11.5:1 were metered separately into a static mixer. The temperatures of the HDI and polyol/butane diol mixture were each  $90 \pm 10^\circ\text{C}$ . A static mixer with all-round heating (model SMX, Sulzer AG) and with a diameter of 6 mm, a length of 6 cm and a rate of shear of  $500 \text{ s}^{-1}$  was used to achieve mixing; the reaction was performed in an extruder at the end.

15

**Example 6 (comparison)**

The test was performed in the same way as in example 5, but HDI was introduced to the reactor at a temperature of  $23^\circ\text{C}$  and the polyol mixture was introduced at a temperature of  $80^\circ\text{C}$ .

20

The results of example 5 and comparison example 6 are given in Table 2. This shows that the TPU produced by the process according to the invention has improved melting characteristics. The low scatter among individual values of the melt flow index MFI within one measurement for the product prepared according to the invention may be taken to indicate a high degree of homogeneity.

25

**Table 2**

	<b>Example 5</b>	<b>Example 6 (comparison)</b>
Recrystallisation temperature $T_c$ [°C]	68	78
Melting point (°C)	180	190
Melt flow index MFI * (190°C)[g/10 min]	49.6±2	55 (scatter 32-60)

\* measured in accordance with ASTM D1238.

5

**Examples 7-10**

TPU formulation:

- 10      1.0 moles      polybutylene adipate,  $\overline{M}_n=840$  g/mole  
          1.3 moles      1,4-butane diol  
          2.3 moles      MDI  
          200 ppm      tin dioctoate (with respect to polybutylene adipate)  
          0.2 wt.%      Loxamide (with respect to the total amount of TPU)

- 15      The components were metered into an extruder of the ZSK 83 type, which operated at a speed of 300 rpm and had a throughput of 600 kg/h. The temperature profiles set via the housing temperatures of the extruder are given in Table 3. In examples 7-9, MDI was metered into the first housing and the polyol mixture consisting of polybutylene adipate and 1,4-butanediol was metered into the fifth housing in the
- 20      extruder. The temperature of the MDI in example 7 was about 60°C, in example 8 about 120°C, in example 9 about 130°C. In example 10, the MDI was heated to 130°C, the polyol mixture to 140°C, then both reactant streams were fed into the first housing. The catalyst was added to the polyol mixture each time, loxamide was admixed with the isocyanate.

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**Table 3: Pre-set screw housing temperatures**

Example	7	8	9	10
Housing 1	80°C	140°C	140°C	none
2	80°C	140°C	140°C	none
3	80°C	140°C	140°C	none
4	none	140°C	140°C	none
5	none	none	none	none
6	none	none	none	none
7	none	none	none	none
8	none	none	none	none
9	none	none	none	none
10	none	100°C	100°C	100°C
11	none	100°C	100°C	100°C
12	150°C	120°C	120°C	100°C
13	100°C	120°C	120°C	100°C
Head	200°C	200°C	200°C	200°C

Films were prepared from the products obtained using an extrusion blow moulding plant. The TPU granulate was melted in a single shaft extruder model 30/25D Plasticorder PL 2000-6 (Brabender Co.) (rate of addition 3 kg/h, temperatures 185-205°C) and extruded through a film blowing head to give a tubular film. The 100 % modulus of the product was determined in accordance with DIN 53504/NSI. The results are given in Table 4.

**Table 4**

Example	Temperature polyol mixture	Temperature MDI	Film properties: specks/structure	100% modulus
7*	150°C	50°C	many/very obvious	12
8*	140°C	120°C	some/obvious	11
9	140°C	130°C	very few/very little	11
10	140°C	130°C	none/none	11

\* Comparison example, not according to the invention

Claims

1. A process for the continuous preparation of thermoplastic polyurethane elastomers in which
- 5 one or more polyisocyanates (A) and
- a mixture (B), with Zerewitinoff-active hydrogen atoms, comprising
- 10 B1) 1 to 85 equivalent-%, with respect to the isocyanate groups in (A), of one or more compounds with on average at least 1.8 Zerewitinoff-active hydrogen atoms and an average molecular weight  $\overline{M}_n$  of 450 to 10000,
- 15 B2) 15 to 99 equivalent-% (with respect to the isocyanate groups in (A)) of one or more chain lengthening agents with an average at least 1.8 Zerewitinoff-active hydrogen atoms and a molecular weight of 60 to 400, and
- 20 0-20 wt.%, with respect to the total amount of TPU, of further auxiliary agents and additives (C)
- are homogeneously premixed in a reactor within a period of at most 5 seconds, wherein the difference between the temperatures of components
- 25 (A) and (B), before entering the reactor, is  $<20^{\circ}\text{C}$ .
2. A process according to Claim 1, in which the temperature of components (A) and (B) before entrance to the reactor is between  $60^{\circ}\text{C}$  and  $220^{\circ}\text{C}$ .
- 30 3. A process according to Claim 1, in which the reactor is a static mixer.

4. A process according to Claim 3, characterised in that the static mixer has a length to diameter ratio in the range from 8:1 to 16:1.
5. A process according to Claim 1, in which the reactor is a twin shaft extruder.
- 5 6. A process according to Claim 1, in which the mixture obtained is reacted in an extruder or a tubular reactor to give thermoplastic polyurethane elastomers.
- 10 7. Thermoplastic polyurethane elastomers prepared according to the process in accordance with Claim 1.
8. Use of the thermoplastic polyurethane elastomers prepared in accordance with Claim 1 for preparing films, laminates, calandered products, hot melt adhesives and powder-slush coextruded products.
- 15

**Process for preparing thermoplastic polyurethane elastomers**

**A b s t r a c t**

Process for the continuous preparation of thermoplastic polyurethane elastomers with improved homogeneity and improved melting characteristics in which

one or more polyisocyanates (A) and

a mixture (B), with Zerewitinoff-active hydrogen atoms, consisting of

B1) 1 to 85 equivalent-%, with respect to the isocyanate groups in (A), of one or more compounds with on average at least 1.8 Zerewitinoff-active hydrogen atoms and an average molecular weight  $\overline{M}_n$  of 450 to 10000,

B2) 15 to 99 equivalent-% (with respect to the isocyanate groups in (A)) of one or more chain lengthening agents with an average at least 1.8 Zerewitinoff-active hydrogen atoms and a molecular weight of 60 to 400, and

0-20 wt.%, with respect to the total amount of TPU, of further auxiliary agents and additives (C)

are homogeneously premixed in a reactor within a period of at most 5 seconds, wherein the difference between the temperatures of components (A) and (B) is  $<20^{\circ}\text{C}$  before entering the reactor.

**COMBINED DECLARATION AND POWER OF ATTORNEY**

ATTORNEY DOCKET NO

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name. I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought

on the invention entitled

**"METHOD FOR PRODUCING THERMOPLASTIC POLYURETHANE ELASTOMERS"**

the specification of which is attached hereto,

or was filed on **December 1, 1998**

as a PCT Application Serial No. **PCT/EP98/07753**

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims.

I acknowledge the duty to disclose information which is material to the patentability of this application in accordance with Title 37, Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s), the priority(ies) of which is/are to be claimed:

**197 55 545.4**  
(Number)

**Germany**  
(Country)

**December 13, 1997**  
(Month/Day/Year Filed)

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose the material information as defined in Title 37, Code of Federal Regulations, §1.56 which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

(Application Serial No.)

(Filing Date)

(Status)

(patented, pending, abandoned)

(Application Serial No.)

(Filing Date)

(Status)

(patented, pending, abandoned)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

**Le A 32 563-US**

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